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Araştırma Makalesi

Investigation of Mechanical Properties of Ti6Al4V Alloy Foams produced by Powder Metallurgy Method

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ABSTRACT

In this study, it was aimed to production titanium alloy implants, which are widely used in the biomedical industry, as foamed materials under different mechanical alloying and sintering conditions using the powder metallurgy method Tİ6Al4V alloy is good mechanical properties, good biocompatibility properties and good corrosion resistance used as hard tissue replacements and implants. Similar mechanic properties with bone are expected from the implant to work coherently for long cycles of use and without any failure. Especially, elastic modulus of implant must be similar with bones, if not, some damages at bone surface and fallowing repeats of implant surgeries are reported. This situation has a destructive effect on health, finance, and comfort of the patient/user of the implant. In this study, powder metallurgy and space holder removal methods were used to produce porous Ti6Al4V specimens. Throughout the project study different space holder materials and binder agents were used. As weight percent, 20%, 30%, 40%, 60%, 70%, 80% porous specimens were pressed at uniaxial press machine, and sintered to the 850 ºC at argon atmosphere in furnace to reduce the oxidation to the level as low as possible. The E-Modulus values of the specimens reached the desired values with increasing porosity. It was obtained as 88 MPa in the specimen with 80% porosity, decreasing inversely proportionally, especially from the 60% porosity rate.

***Keywords**: Foam, Sintering, Powder metallurgy, Ti6Al4V, Implant*

Toz metalurjisi Yöntemi ile Üretilen Ti6Al4V Alaşımlı Köpüklerin Mekanik Özelliklerinin İncelenmesi

Öz

Bu çalışmada biyomedikal endüstrisinde yaygın olarak kullanılan titanyum alaşımlı implantların toz metalurjisi yöntemi kullanılarak farklı mekanik alaşımlama ve sinterleme şartlarında köpüklü malzeme olarak üretilmesi amaçlanmıştır. Ti6Al4V iyi mekanik özellikleri, biyo-uyumluluğu ve iyi korozyon direnci gibi özellikleri sebebiyle sert doku implantları olarak kullanılmaktadır. Kemik dokusu ile çalışacak implant malzemesinin mekanik özelliklerinin kemiğe benzer olması, kemik ve implantın uyumlu ve uzun döngü süreleri boyunca kullanılabilmeleri için tercih edilmektedir. Bilhassa, implantın elastik modülünün kemiğin elastik modülüne yakın olmadığı takdirde, kemiğin zarar gördüğü ve ilişkili ortopedik ameliyat ve operasyonların tekrar edildiği rapor edilmiştir. Bu durum hem ekonomik olarak hem de implant kullanıcısının konforu ve sağlığı açısından yıkıcı etkilere sahip olabilmektedir. Bu çalışmada toz metalurjisi ve boşluk yaratıcı malzemelerin uçurulması prensipleri

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kullanılarak poroziteli Ti6Al4V numuneleri hazırlanmıştır. Farklı uçucu malzemeler ve bağlayıcılar denenmiştir. Ağırlıkça yüzde porozite miktarları %20, %30, %40, %60, %70, %80 değerlerinde üretilen numuneler tek eksenli sıkıştırma yöntemiyle presslenerek, oksidasyonu en az değere düşürmek amacıyla argon ortamında 850 ºC' ye kadar sinterlenmiştir. Numunelerin E-Modül değerleri artan porozite ile birlikte istenilen değerlere ulaşmıştır. Özellikle %60 porozite oranından itibaren ters orantılı olarak azalarak %80 poroziteye sahip numunede 88 MPa olarak elde edilmiştir.

Anahtar Kelimeler: *Köpük, Sinterleme, Toz metalurjisi, Ti6Al4V, İmplant*

I.INTRODUCTION

Titanium was first discovered as an element in 1790. The element titanium provides low density, good rigidity, and very good biocompatibility. In addition, with its good plasticity, mechanical properties and improved corrosion resistance, its usage areas are quite wide. Titanium and Ti6Al4V alloy are widely used in medicine, biomaterials, automotive, shipbuilding, architecture, aircraft construction [1,2]. It is an element that is needed in many important industries as well as in the pharmaceutical industry. As a result of recent tests on titanium and its alloys, it has been discovered that it has a very good compatibility with the human body due to the thin TiO2 (titanium oxide) layer formed on the surface. Therefore, these materials are in high demand as biomaterials recently. They are preferred because of their high biocompatibility, very good corrosion resistance and bone-like mechanical properties [3]. In recent years, Ti and Ti6Al4V alloys have been used mostly as rigid and hard bone tissue implants. Again, due to their very good mechanical properties, they are preferred as an alternative implant material for many steel types. It is an important factor that titanium and its alloys give better results than materials used for the same purpose, especially the modulus of elasticity [1,4].

As well-known there is no perfect engineering material for any application, the major issue about hard tissue replacement is called stress shielding effect. Stress transfer of alternative materials to be used instead of bone is very important. Here, titanium alloy implants used instead of bone. It has been determined that they transfer stress close to the properties of the bone. Therefore, stress protection takes place. On the contrary, different stress conditions cause fracture of bone or implant materials in the body [5]. Products are created by Powder metallurgy using the basic process consists of arranging composition by mixing main material and additive materials, mixing them, compacting with some devices like uniaxial pressing and heat treating them [6]. Powder metallurgy has many advantages as well as great economic advantages. The production of these products is carried out using powder molding methods and devices. In addition, the process in question stands out as a manufacturing method that provides a very economical advantage with faster and less wastage in achieving the desired alloy and microstructure for production [7]. Space holder method is the method that is used for creating porous structured materials, by adding volatile materials such as carbamide. After pressing of the material these volatile materials escape from the specimen and leaves porosity behind in their location [8]. Especially in the development of materials to be used as manufacturing for the human body, hollow materials are of great importance. Hollow materials are also referred to as foamed materials in the literature. In this method, there are several steps to obtain a hollow structure. As in the powder metallurgy process: selection of the powder type to be worked on, mixing, compaction, removal of the spacer and sintering processes take place. First, metal and foaming (space-creating) powders should be selected. Then mixing is done with appropriate mechanical alloying parameters to ensure homogeneity. Here, in order for the powders to be mixed well, the mentioned parameters (Mixing time, speed, mixer quality and quantities) are very effective on the process. How well the powders are mixed depends on these parameters. Then, the mixture obtained as a result of mechanical alloying is compressed in the appropriate device under the appropriate pressure and in the appropriate mold. Depending on how and what kind of spacer is used in the mixture obtained because of mechanical alloying, the next stage is passed. This stage is defined by sintering. The spacer is removed with the determined sintering temperature, time, and atmosphere or with some solutions. and space is obtained in the structure [9,2]. Metal foams, which have been produced on account of scientific studies in recent years, have begun to be used in many areas. It is used as a filter in advanced technological processes and as a biomedical implant in the field of health, especially with its energy absorption and temperature changing feature. Therefore, the spacer technique has begun to be used. This production method is suitable for obtaining a highly porous and open cell structure suitable for medical implants. It exhibits a bone-like structure to be used as an implant instead of the metal foams produced. In addition, by increasing the said porosity, mechanical properties can be obtained according to the desired properties [10]. Advantages of metal foams over other materials; It is to take an active role in the transfer of body fluid by connecting to the surrounding tissues through the condensation of the tissue to be used as an implant towards the cavities. transporting the body fluids in question is a very critical stage. Unsuitable metallic implants cause problems from time to time due to their mechanical properties that are not compatible with bone. Various methods are used to overcome this. By increasing the porosity of said materials, the Young's modulus is reduced. By regulating the porosity rate in foamed metals, the stress protective effect between the implant and the bone is tolerated. Therefore, the hardness value of the material is controlled to the desired rate. For the biocompatibility of Implants to be used in the human body, low density (high porosity), good corrosion resistance, good wear resistance and sufficient strength are. Among these, the most used implant materials are pure titanium and Ti6Al4V alloy [11].

The most ideal implant to be used in the human body should be very biocompatible. In other words, it is expected that the cell density, which we call negative tissue response, should not be low. It should have a low/suitable density, suitable/high mechanical properties and suitable fatigue resistance for various activators, a low modulus of elasticity and very good wear resistance, as is the density of the bone type found in the human body. It is very difficult to meet all these features with only one material. The production of implant material with this feature is very important and groundbreaking [12]. As it is known, the main disadvantage of the metals we use is that they corrode incompatible with the living tissue and do not adapt to the tissue. Many metal materials can be tolerated in the human body in small amounts, even as metallic ions. Tissue incompatibility in the human body, namely corrosion, adversely affects the implant applied to the body, resulting in the fragmentation of the implant, and adversely affecting the surrounding tissues and organs [3,13]. In addition, there is a slow growth of hydrated TiO2, which leads to the combination of calcium and phosphorus on the surface of the Ti implant. This characteristic feature has led to speculation regarding a potential bioactive behavior. [14,15]. In particular, the formation of a TiO2 layer on the surface of titanium and its alloys is a factor that increases the biocompatibility between the body and the implant material. (TiO2) It is an implant with high surface energy. At the end of the implant placement operation, titanium shows a positive response with the direct adaptation of the minerals to the bone-titanium interface. This layer provides a positive body reaction leading to body and implant integration [16]. Especially Ti biomaterials are not rejected by the body and establish good physical connections with the bone. Titanium particles also have specific biological effects on white blood cells in vivo. Highly porous Ti and Ti6Al4V are preferred in the implant industry due to their excellent biocompatibility, low densities, and passive titanium oxide layer formation when in contact with oxidizing media [5,16,17]. Due to these properties, Ti6Al4V alloy is indispensable and widely preferred in implant use [17,18]. As a result, good properties of titanium and its alloys were considered in this study. In addition to these features, considering the positive effect of foam formation on implant application, titanium and its alloys were selected for biomedical applications [19,20].

II.MATERIALS AND METHODS

Titanium powders (Alfa Aesar, USA) to be used for the foams to be produced in the experimental study and space forming powder metallurgy method were produced. The chemical composition of titanium powder is by weight (99.61% Ti, 0.23% O, 0.018% N, 0.03% Fe, 0.01% Mn, 0.01% Mg, 0.009% C, 0.01% Al, 0.01% Cl, 0.01% Na and 237 ppm). H). Average particle size of the powder used particle sizes averaged 44 micrometers. Carbamide (Merck, Germany) with irregular structure and dimensions of 710-1000 μm was used as a spacer. for high density and strength polyvinyl alcohol (PVA) was used as binder (Merck, Germany). The metallic powders were mixed with 1.5% by weight PVA under mechanically determined conditions. For the implants production, to obtain human like bone structure, the production processes were meticulously applied in the literature. The Young's modulus and yield strength values of porous specimens must match those of the human bone tissue, which are stated as being in the ranges of 0.09-1.5 GPa and 40-

150 MPa, respectively, according to the example researchers [20]. Spherical Ti6Al4V alloy powders (average particle size ~ 40 µm) were used as a main component in this experiment. Polyacrylonitrile (PAN) (average particle size 100 micron) was chosen as a space holder material polyvinyl alcohol PVA and, paraffin were used as space holder for mixture respectively. Unfortunately, all of the specimens were failed and not formed as a foam. All of the types of space holder and binder mixtures are shown in the table below. The possible reasons for these failures are argued in chapter.

Table 1. *Materials used in experiments*

Experimantal No	**Main Component**	**Space Holder**	**Binder**	**Result**
1	Ti-6Al-4V	Carbamide	PVA	Fail
2	Ti-6Al-4V	PVA	-	Fail
3	Ti-6Al-4V	PVA	Paraffin	Fail
4	Ti-6Al-4V	Carbamide	PAN	Fail
5	Ti-6Al-4V	PAN	-	Succeed

Experimental Equipments: Used equipments in this thesis work are listed below; one axial pressing machine, Tubular powder mixing device, Sintering furnace (argon atm), Density measurement device, Instron test device. The devices used during the experimantal study are shown in Figure 1 (a), (b) and Figure 2 (a), (b), (c).

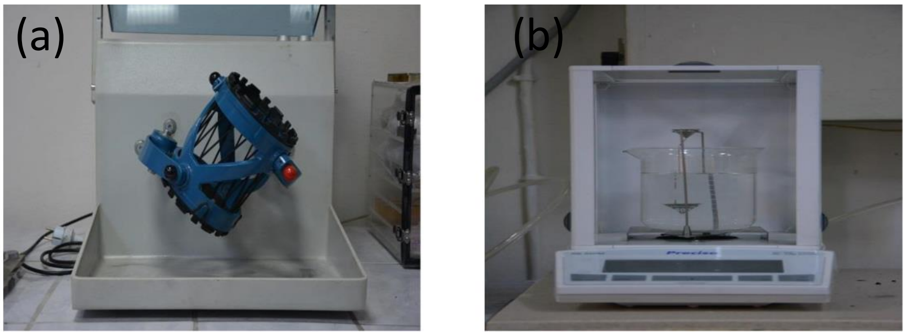

***Figure 1**. **(a)**Turbula powder mixing device and, **(b)** Density measurement device.*

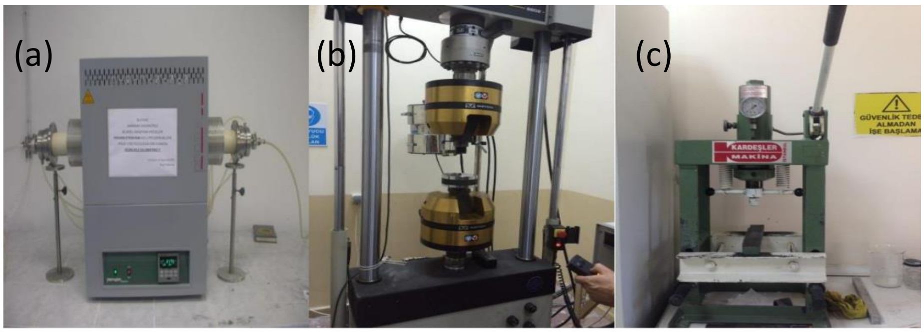

***Figure 2. (a)** Sintering Furnace, **(b)** One Axial Pressing and **(c)** Compression Test Device*

III.EXPERIMENTAL PROCEDURE

The obtained metallic implant foam samples, Ti6Al4V alloy powders, space formers and binders were produced by mechanical alloying method and void forming method. The average particle size of the particles used in sample production is 40 μm. As a space holder PAN (avarage particle size 100 micron) was used. Ti6Al4V alloy powders are weighed equal amount for each specimens and polyacrylonitrile (Pan) are weighed different proportions according to their porosity ratio for each specimens. As weight percent, 20%,30%, 40%, 60%, 70%, 80% porous specimens were prepared and mixed. Samples obtained by mechanical alloying; It was compressed into pellets in 10 mm diameter molds under 200 bar pressure in a uniaxial press in a hydraulic molding machine. The void formers and PAN binder in the pellet samples obtained were subjected to sintering in a horizontal tube furnace. Sintering conditions: Firstly, as preheating, it was increased to 200 °C with 2 °C/min speed and left for 1 hour. then it was increased to 850 °C at a speed of 3 °C/min and sintered for 1 hour. Specimens were sintered at temperature 850 °C for 1 hour under high purity argon gas atmosphere in a horizontal tube furnace. The diameter of sintered specimens was between 10- and 8.7-mm. The powder metallurgy production method flow chart is shown in Figure 3.

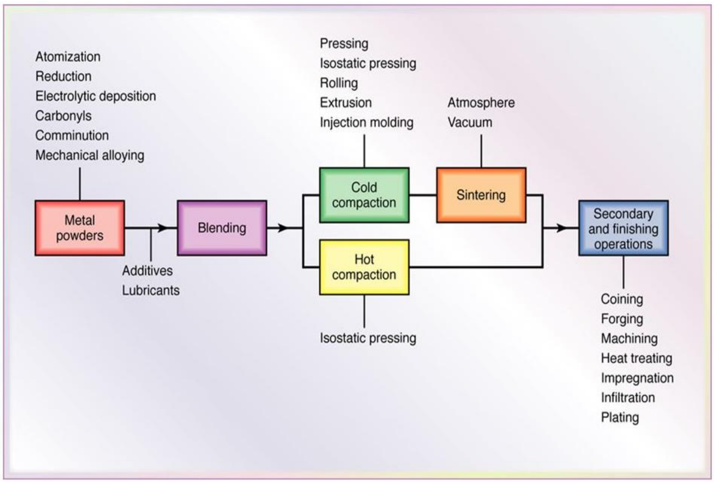

Figure 3. *The powder metallurgy production method flow chart*

Density and mass of sintered specimens were changed depending on the porosity level. Densities of the produced specimens were determined geometrically from the measured weight and dimensions with the aid of density measurement device. Microstructural characteristics of the sintered foams were examined in Light and Stereo Microscopes. Mechanical characterization of the samples was carried out by compression tests performed on a Instron compression testing machine. The stress strain obtained as a result of the compression test in the calculation of the mechanical properties of the samples obtained by the powder metallurgy method. Curves were used. In these curves, respectively, belong to each sample. Elasticity modular, yield strength values and deformation amounts were obtained. The said values were calculated from the data obtained from the device computer and the stress-strain curves. The sintering process diagram is shown in Figure 4.

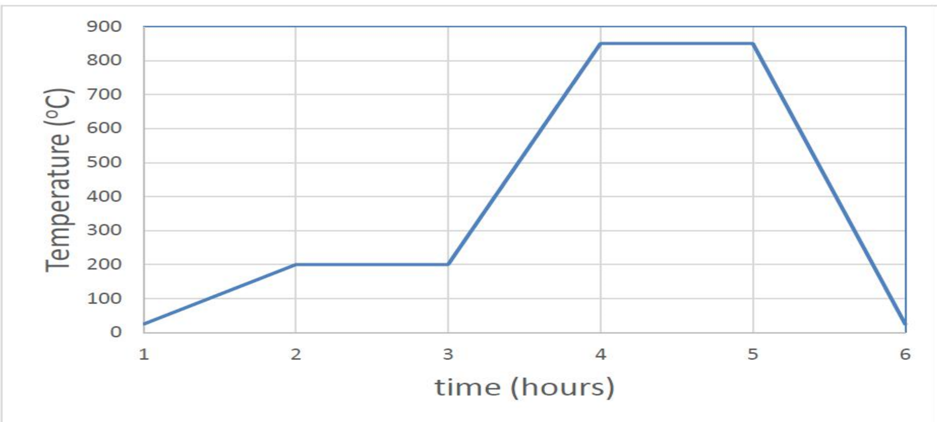

Figure 4. *Sintering Temperature-Time*

IV. RESULTS AND DISCUSSION

In this study, highly porous Ti6Al4V foams with porosity in the range of 20 – 80 %, were produced by powder metallurgy based on space holder technique. Figure 5 and 6 shows the photographs of the sintered Ti6Al4V foams.

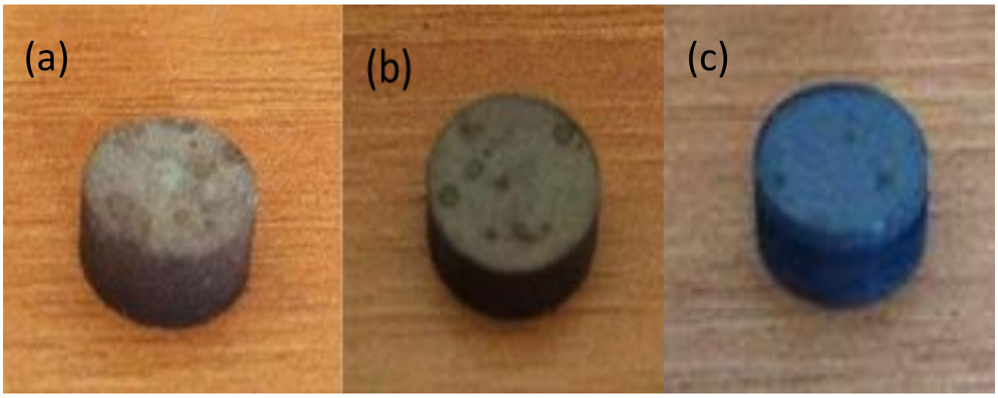

***Figure 5. (a)** 20%, **(b)**30% and **(c)**40% porous specimens*

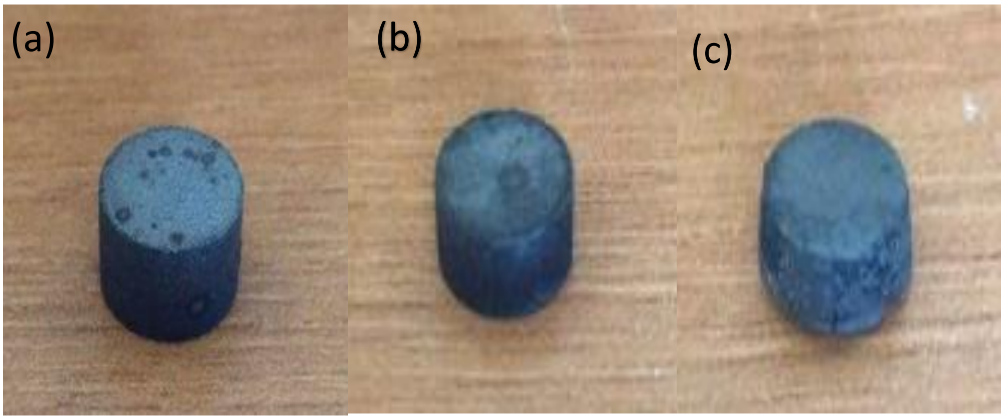

***Figure 6.** (a) 50%, (b) 70% and (c) 80% porous specimens*

A) Results of Density and Porosity Determination

The properties of powders are given in the previous section and the average density values of samples containing different amount of PAN are listed in Table 2.

***Table 2.** Density of foam samples after sintering*

Sample number	**1**	**2**	**3**	**4**	**5**	**6**
Porosity (%)	20	30	40	60	70	80
Diameter (mm)	10	10	10	9	8,8	8,7
Height (mm)	5,35	3,75	7,2	3,95	4,45	3,8
Soaked weight (g)	1,211	0,8	1,469	0,63	0,608	0,354
Suspended weight in	0,908	0,594	1,065	0,431	0,401	0,179
Density g/cm3)	3,99	3,877	3,6	3,16	2,932	2,019

Table 2 shows that the densities of the samples decrease with increasing porosity percent. And also it can be seen from the Table 2, the values of % porosity, diameter and height of the sintered specimens.

B) Results of Microscopic Examination

The microstructure examination of the foamy samples obtained by powder metallurgy method was carried out with an optical microscope. Metallographic images obtained at X500 magnifications it can be seen in Figure 7.

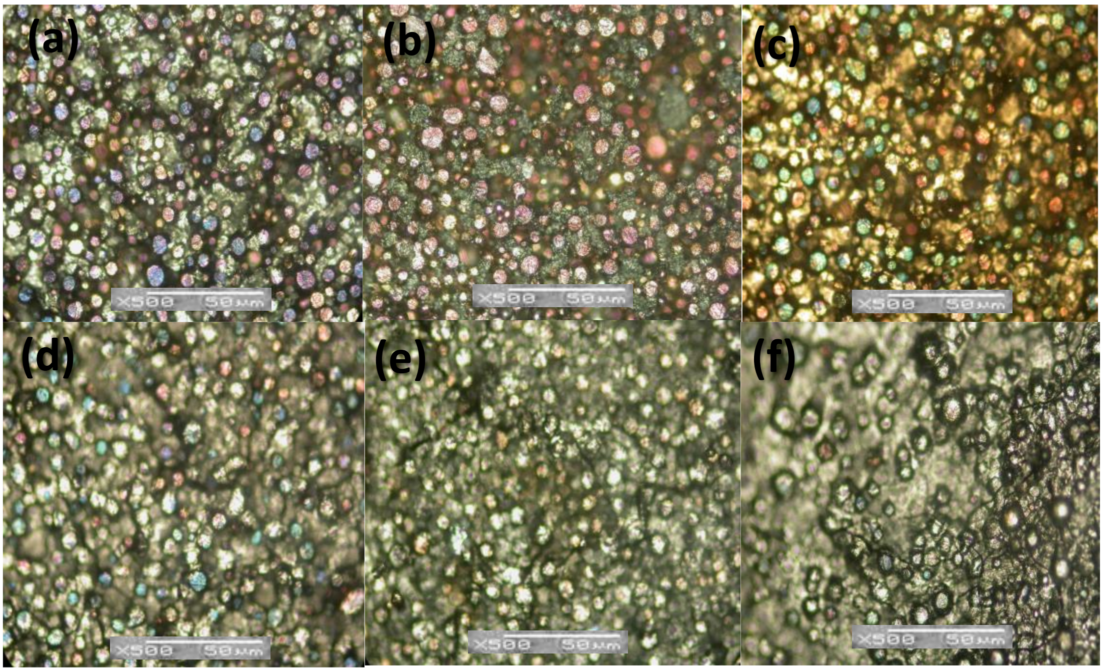

Figure 7. *Ti6Al4V foam with **(a)** 20%, **(b)** 30%, **(c)**40%, **(d)** 60%, **(e)**70% and **(f)** 80% porosity (x500 Magnification)*

C) Results of Compressive Testing

The data obtained from the tensile and mechanical tests (TSEN 138) performed according to the determined standards on the foamed samples obtained by the powder metallurgy method were given in Table 3.

Table 3. *Elastic Modulus of specimens with different porosity percents*

Sample Number	Porosity (%)	Load Failure (N)	Strain Failure (N)	Comprassion Max. (N)	Max Stress (MPa)	EModulus (MPa)
1	20	164,36	32,27	509,4	6,5	300
2	30	142,56	24,85	1168	14,8	348
3	40	285,97	22,81	935	11,9	496
4	60	1199,04	38,34	2190	36,0	554
5	70	977,93	36,83	1498	24,5	452
6	80	467,08	52,47	726	12,0	74

Compressive strength and elastic modulus results obtained as a result of tensile tests performed on foamed samples obtained by powder metallurgy method according to the determined standards. It can be seen in Figure 8 (a) and (b).

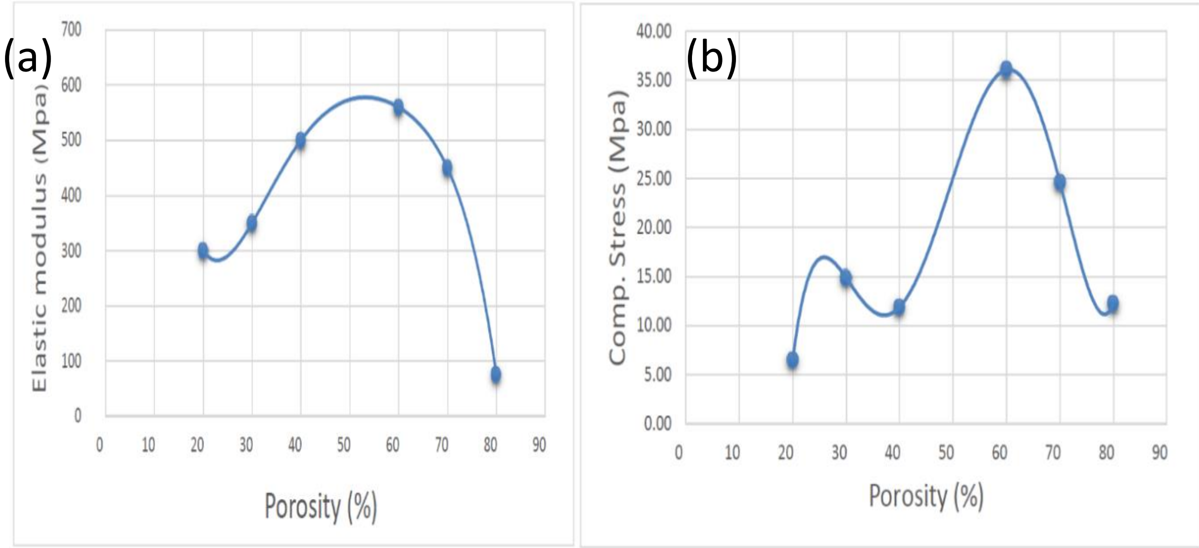

Figure 8. (a) *E- Modulus with different porosity ratio and* ***(b)*** *Compression Stress with different porosity ratio*

The findings of the compression test on the first three samples were unexpected since, in principle, the porosity ratio should increase as the modulus of elasticity decreases [18], but the first three samples demonstrate the opposite relationship. This inaccuracy is most likely the result of human error and is inconsistent with published study. Yet, the final three samples exhibit the behavior that would be predicted by a diminishing elastic modulus. As a result, the examples 4 and 5 were chosen as healthy specimens to comment on [19,20].

V. CONCLUSIONS

- ✓ There were some problems in this study. In the literature review performed again, the problems in the sample preparation phase in creating a porous structure were overcome [18].
- ✓ The differences in powder particle sizes contributed to obtaining the desired E-Module values. As a result, the elastic moduli of the 40%, 50% and 60% specimens decreased as expected as the porosity content increased.
- ✓ It can be said that the porous Ti6Al4V implant material can be made by employing powder metallurgy techniques and space holder technique to construct porous structure by using these results and the prior studies done on stress shielding problem as a reference.
- ✓ As the porosity increases, elastic moduli will be decreased and this will be closer to the bone's mechanical properties, this may eliminate some problems caused by stress shielding effect.
- ✓ In this work, healthy specimens that gives expected decrease in elastic moduli was in the range of 0,45-0,56 GPa and the known values of human bone tissue was in the range of 0,09 – 1,5 GPa. So, it can be concluded that making porous materials for implantation the stress shielding effect can be decreased or eliminated.
- ✓ In this way the negative effects of bone loosening, implant loosening, economical damage can be minimized for both the patient-user and producer of the implant.

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REFERENCES

[1] A. Michael, F. Jones and R.H. David, "Engineering Materials 2" Oxford Pergamon Press. ISBN 0-08-032532-7. Pp.564.1992.

[2] İ. Topcu and E. Karaman, "Çok Duvarlı Karbon Nanotüp Takviyeli Düzenli/ Düzensiz Şekilli Ti-6Al-4V Kompozitlerin Aşınma Davranışlarının İncelenmesi", *Düzce Üniversitesi Bilim ve Teknoloji Dergisi*, c.7, s.3, ss.249-1260, 2019.

[3] İ.Topcu and M Ceylan, "Wear behavior of irregular shape Ti6Al4V powder reinforced with carbon nanotubes", *Journal of Ceramic Processing Research*, vol.21, no.5, pp.539-546,2020.

[4] M. R. Usal , M. Taşlıdere and M. F. Saraç, "Titanyum Karbür (TiC) Takviyeli Epoksi ile Güçlendirilmiş Hibrit Kompozitlerin Çarpma Davranışının Deneysel ve Sayısal İncelenmesi," *Düzce Üniversitesi Bilim ve Teknoloji Dergisi,* c.8, s.1, ss.18-32, 2020.

[5] M. Niinomi and M. Nakai, "Titanium-Based Biomaterials for Preventing Stress Shielding between Implant Devices and Bone", *International Journal of Biomaterials*, vol. 2011, no.836587, 2011. doi. 10.1155/2011/836587

[6] İ.Topcu, "Karbon Nanotüp Takviyeli Alüminyum Matriksli AlMg/KNT Kompozitlerinin Mekanik Davranışlarının İncelenmesi", *Çanakkale Onsekiz Mart Üniversitesi Fen Bilimleri Enstitüsü Dergisi,* sayı 4, no 1, 99-109.2018. https://doi.org/10.28979/comufbed.359796

[7] İ.Mutlu, "Sinter-coating method for the production of TiN-coated titanium foam for biomedical implant applications", *Surface and Coating Technology*, vol.232, no.15, pp. 396-402, 2013. doi.org/10.1016/j.surfcoat.2013.05.041

[8] İ.Topcu and M Ceylan, "Wear behavior of irregular shape Ti6Al4V powder reinforced with carbon nanotubes", *Journal of Ceramic Processing Research*, vol.21, no.5, pp.539-546,2020.

[9] M. Ashby, A. Evans, N. Fleck, L. Gibson, J. Hutchinson and H. Wadley, "Metal Foams: A Design Guide", eBook ISBN: 9780080511467, *Elsevier Science*, Boston, MA, 2000.

[10] K. S. Won, J. Hyun-Do, K. Min-Ho, K. Hyoun-Ee, K. Young-Hag and Y. Estrin, "Fabrication of porous titanium scaffold with controlled porous structure and net-shape using magnesium as spacer", *Materials Science and Engineering C*, vol. 33, n.5 pp. 2808–281,2013.

[11] I. Topcu, "Determination of the mechanical properties of al/mwcnt composites obtained with the reinforcement of cu-coated multiwall carbon nanotubes (MWCNTs)", *Materiali in Tehnologije*, vol.54, n.5, pp.689-695,2020.

[12] C. Oldani and A. Dominguez, "Titanium as a Biomaterial for Implants," ISSN. 978-953-307-990-5. pp.628, 2012. doi.10.5772/27413

[13] İ. Topcu,B. N. Çetiner, A. N. Güllüoğlu and G. Özkan, "Investigation of Creep Behavior of CNT Reinforced Ti6Al4V Under Dynamic Loads",*J.Chem.Soc.Pak.*, vol.42, n.1, pp.70-80, 2020.

[14] İ.Topcu, M Ceylan and E, B Yilmaz, “Experimental investigation on mechanical properties of Multi Wall Carbon Nanotubes (MWCNT) reinforced aluminium metal matrix composites”, *Journal of Ceramic Processing Research*, vol.21,n.5, pp.596-601,2021.

[15] M. Y. Zakaria, A.B. Sulong, M. I. Ramli and M. R. Raza, “Determination of Critical Powder Loading of Titanium-Hydroxyapatite with Powder Space Holder for Powder Injection Molding Feedstocks”, *Journal of Mechanical Engineering*,vol. n.1, pp.11-21, 2017.

[16] O. Bazaka, K. Bazaka, P. Kingshott, R. J. Crawford and E. P. Ivanova, “Metallic-implant biomaterials”, *Materials-Science-and-Engineering-Reports*., ch1, pp.98, 2015.

[17] A. Mansourighasri, N. Muhamad and A. Sulong."Processing titanium foams using tapioca starch as a space holder" *Journal of Materials Processing Technology*, vol.212, n.1, pp.83-89,2012

[18] İ.Topcu “Investigation of Wear Behavior of Particle Reinforced AL/B4C Composites under Different Sintering Conditions” *Journal of Technical Glasnic*, vol. 14, n.1, pp. 7-14,2020.

[19] M. R. Usal, M. Taşlıdere and M. F. Saraç , "Titanyum Karbür (TiC) Takviyeli Epoksi ile Güçlendirilmiş Hibrit Kompozitlerin Çarpma Davranışının Deneysel ve Sayısal İncelenmesi," *Düzce Üniversitesi Bilim ve Teknoloji Dergisi*, c.8, s.1, ss.18-32, 2020. doi:10.29130/dubited.606515

[20] İ.Topcu “Examination of wear properties of Al/B4C composites reinforced with irregularly shaped B4C” Journal of Ceramic Processing Research vol 22 no 3, pp. 276-282, 2021.